

**Polymerizable Derivatives of Long-Chain Fatty Acids****I&EC—March 1955****Vinyl Stearate and Copolymerization of Vinyl Chloride with Other Vinyl Esters**

As a part of a general study of the utilization of fatty derivatives in plastics, copolymers of vinyl chloride with vinyl stearate and other vinyl esters were prepared and their mechanical, thermal, viscoelastic, and viscous properties were determined. The study was undertaken to determine whether true plasticization (impartation of flexibility without irrecoverable flow) could be achieved by copolymerization and whether the length of the acyl chain of the comonomer affects the efficiency of internal plasticization.

Copolymers of vinyl chloride containing less than about 25% vinyl stearate have improved properties in some respects as rigid vinyls, because they have lower milling temperatures and a lower melt viscosity-temperature coefficient. Copolymers containing 30 to 50% of vinyl stearate are flexible and resemble compositions of polyvinyl chloride and external plasticizers in their mechanical and thermal characteristics.

Both the rigid and flexible types may be useful for extrusion, because they are preplasticized. A long acyl chain is desirable because as the acyl chain length is progressively decreased from C<sub>18</sub> to C<sub>2</sub>, the internal plasticizer efficiency decreases progressively.

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# Polymerizable Derivatives of Long-Chain Fatty Acids

## VINYL STEARATE AND COPOLYMERIZATION OF VINYL CHLORIDE WITH OTHER VINYL ESTERS

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### These copolymerization studies present

- . . . information on mechanism of plasticization
- . . . preplasticized polymers, both rigid and flexible

MUCH work has been done on the preparation and testing of compositions of plasticizers and polyvinyl chloride. In most cases, such mechanical mixtures are subject to compositional changes because of volatilization, migration, and/or leaching of the plasticizer. For both practical and theoretical reasons, it would be desirable to determine whether it is possible to prepare a copolymer of vinyl chloride which would have properties closely resembling plasticized polyvinyl chloride. From the practical point of view, such a copolymer would be free from the problems of migration and evaporation of plasticizer. From the fundamental point of view, a systematic study of copolymer systems for this purpose might yield information concerning the mechanism of plasticization.

Certain phenomena, which must be accounted for in any unified theory, have been generally recognized to occur when polyvinyl chloride is plasticized. The extent to which the same events occur when polyvinyl chloride is modified by copolymerization may be used as a means of comparing the two methods of plasticization and deciding whether the same mechanism is operating.

Space limitations prevent an exhaustive review of the phenomena and proposed theories associated with plasticization. A number of these were selected to show the relationship between external and internal plasticization.

### PHENOMENA OBSERVED

The modulus of elasticity at a given temperature is reduced as the plasticizer content is increased. In a homologous series, a plasticizer of low molecular weight is less effective, on a molar basis, in reducing the modulus of elasticity than is a high molecular weight member of the series. [Data for such a calculation are presented by Lawrence and McIntyre (21) for the homologous dialkyl phthalates.] For a given composition, the modulus increases as the temperature decreases. In a narrow temperature range characteristic of the amount and the kind of plasticizer, the modulus increases first rapidly and then more slowly

dimensional change which results at failure are changed by varying the plasticizer content. For example, the tensile strength is reduced and the per cent elongation is increased as the amount of plasticizer is increased.

As the plasticizer content is increased, the nature of the response to deformation (short of failure) changes. When plasticizer is absent or is present in low concentrations, recovery from deformation may be almost entirely instantaneous. With increasing plasticizer concentration, there is an increasing amount of delayed elastic recovery. For small deformations, complete dimensional recovery may occur even at plasticizer concentrations as high as 90% (7). (There is implied a variation in the amount of work of deformation done via several molecular methods of deformation.)

Plasticized compositions held at a constant low stress at constant temperature may elongate indefinitely (8). Full dimensional recovery from creep is observed when the stress is removed. Plasticizers vary in their effect on the first and second derivatives of creep with respect to time. In some cases, the first and second derivatives are affected both by plasticizer concentration and by temperature, but the gross qualitative effect is a horizontal shift of the time scale of the creep curves [(7, p. 183), but compare data in this paper and in (8, p. 220) for the detailed quantitative effect].

There is a greater rate of decay of stress than of birefringence in stress relaxation and birefringence measurements (8) on plasticized compositions. If a sample of a plasticized composition is held at a constant elongation at constant (equilibrium) temperature until a constant stress is attained and the temperature is then decreased, both the stress and the birefringence decrease reversibly with the temperature, provided that the initial equilibrium temperature is not exceeded. If it is exceeded, the stress and birefringence decrease irreversibly, and a new reversible pattern of change in stress and birefringence with temperature arises having its maximum values at the new initial equilibrium temperature.

The second-order transition temperature of a plasticized composition decreases as the plasticizer content increases (11). Plasticizers vary in their efficiency in decreasing the second-order transition temperature.

Plasticizers vary in their ability to solvate the polymer into which they are incorporated. If the  $\mu$  value of the plasticizer is taken as a measure of solvation power (11), there is a relationship between solvation power and plasticizer efficiency as measured by the lowering of the second-order transition temperature. The efficiency passes through a minimum at  $\mu \sim 0.4$ .

The dielectric constant of plasticized compositions of polyvinyl chloride varies directly with the temperature and the plasticizer concentration and inversely with the frequency. The

ture and reaches its maximum at a temperature characteristic of the composition and the frequency. As the frequency is increased or the plasticizer content is decreased, the temperature at which the maximum occurs increases (14, 22). The amount of plasticizer required to produce a given electrical effect—e.g., the maximum power loss factor—depends on both the number of plasticizer molecules and their size and shape. For a given molar concentration, a plasticizer of high molecular weight or of cylindrical shape is more effective than one of low molecular weight or spherical shape. The frequency of maximum electrical loss tangent and the frequency of maximum mechanical loss tangent both shift the same amount with change in temperature. This leads to the conclusion that the activation energies for the two processes are the same (19).

Several theories have been proposed to show the interrelationship among these phenomena and, in some of the theories, to relate the macroscopically observed behavior to some molecular mechanism. Although none of these theories has completely resolved the mechanism of plasticization, they are very valuable in connection with the problem posed in this paper—can plasticization be achieved by copolymerization? These theories permit predictions regarding the behavior of a nonmobile plasticizer and the extent to which the various phenomena should be observed in internally plasticized polymers.

#### THEORIES PROPOSED

Alfrey and coworkers (7, 8) propose the existence of two distinct regions in polyvinyl chloride: a crystalline region consisting only of polyvinyl chloride and an amorphous region consisting of polyvinyl chloride (and plasticizer when present). The plasticizer facilitates the micro-Brownian movement of polymer segments permitting segmental motion, while the crystallite region holds the polymer in a three-dimensional gel network preventing true (irrecoverable) flow. Two possible mechanisms of plasticizer-polymer association are presented; existing evidence does not permit the selection of a more probable one. In the dynamic mechanism, the mean lifetime of association is small compared to the time required for a segmental jump, and the facilitation of micro-Brownian movement is due to the dynamic equilibrium of solvation, desolvation, and diffusion of the plasticizer. On the other hand, it is possible that the mean lifetime of association is large compared to the time scale of segmental motion, and static shielding ensues. "The softening action would then result from the fact that a copolymer of naked and shielded dipoles would be more flexible than the polar polymer alone" (7).

If the theories of Alfrey and his coworkers are accepted, important deductions may be made concerning the possibility of achieving internal plasticization and the extent to which this type of plasticization may approach external plasticization. A key point in these theories is the maintenance, after plasticization, of the three-dimensional gel network due to the crystallite regions. Plasticization would appear to be impossible in a totally amorphous polymer (unless a means of cross linking other than crystallites exists) and, to the extent that internal plasticization destroys crystallinity, it will resemble true plasticization less and viscous flow more. Because the crystallite regions are not penetrated, these theories require a nonuniform distribution of the plasticizer through the polymer. In a copolymer the distribution of the comonomer would be expected to be more nearly homogeneous than the distribution of a plasticizer through a polymer. As the position of the comonomer is predetermined, it cannot segregate preferentially in the amorphous regions and, therefore, by applying this theory, one may predict that in internal plasticization greater interruption of crystallites occurs, yielding a copolymer which has a weaker three-dimensional network and a more compliant structure and exhibits more viscous flow. However, because the extent of plasticization is roughly proportional to the weight per cent of plasticizer present, a copoly-

mer of vinyl chloride and a comonomer having a long side chain—e.g., vinyl stearate—should exhibit less flow than a copolymer containing the same weight of comonomer having a short side chain—e.g., vinyl acetate—since the number of groups interrupting crystallinity will be fewer in the former.

The crucial aspect of the theories of Alfrey and coworkers, especially with reference to the possibility of internal plasticization, is the mechanism of association of plasticizer and polymer. If a dynamic mechanism is necessary—that is, if the facilitation of segmental motion is due to the solvation-desolvation-diffusion process—it may be predicted that internal plasticization is impossible, and that, at best, copolymers should exhibit only viscous flow. The static theory, as the authors implied, has a copolymer system as its extreme form.

Boyer and Spencer (11) propose that the lowering of the temperature at which chain segments rotate about a carbon-to-carbon bond is the cause of the phenomena observed in plasticization. The difference in efficiency among plasticizers is due to the differences in solvating power (as measured by the  $\mu$  value). The least efficient plasticizer is one in which there is little energetic difference between a polymer-to-plasticizer and a polymer-to-polymer contact ( $\mu$  about 0.4). The behavior of plasticizers having a  $\mu$  value above about 0.4 follows a different plasticizer mechanism than those below about 0.4. As plasticizers having a high negative  $\mu$  value are the most efficient and are considered by Boyer and Spencer to resemble internally plasticized copolymers as a limiting case, one may, perhaps, conclude that according to this theory some copolymers should exhibit true plasticization.

Zhurkov (28) proposes the existence of "active groups" in polymer chains whose interassociation ("node" formation) causes polymer "solidification"—i.e., the passage from a rubbery state (low modulus) to a glassy state (high modulus). A plasticizer functions by associating with and thereby shielding the active groups and preventing them from forming nodes. This lowers the temperature (second-order transition temperature) at which the system possesses sufficient thermal energy to disrupt a large number of the nodes present. According to Zhurkov, "the fall in the temperature of solidification is proportional to the number of sorbed molecules irrespective of their chemical nature."

As Zhurkov's theory does not require dynamic behavior of the plasticizer, it does not rule out internal plasticization. It predicts, however, that all types of comonomer units which do not form nodes of high association energy will be equally effective in plasticization.

Doolittle (16) presents a molecular mechanism for plasticizer action which is akin to the Zhurkov theory in its concept of the shielding of active centers. The experimental evidence which Doolittle advances for his theory demonstrates a difference in efficiency among plasticizers which can be ascribed to the chemical nature and, in a homologous series, to the molecular size and shape of the plasticizer. Both Doolittle and Boyer and Spencer relate plasticizer efficiency to solvation power. The former uses the threshold concentration and the latter the  $\mu$  value as the criterion of solvation power.

Fuoss (22) considers plasticization to be a process of reduction of internal viscosity of polymer molecules by association of the plasticizer with the polymer chain. From the observation that a plasticizer which produces a small specific volume change (in the polymer-plasticizer composition) is more effective in producing a given electrical response than is a plasticizer which gives rise to a large specific volume change, Fuoss concludes that a plasticizer which is strongly associated with the polymer chain is more effective. A logical extension of this approach would seem to include copolymerization as a method of plasticization.

Each of these theories of the mechanism of plasticization, with the exception of the dynamic mechanism of association of Alfrey and coworkers, has, as a part, the concept of a strong, long-time

association of the plasticizer with the polymer chain. It is the authors' hypothesis that internal plasticization by copolymerization is the ultimate extension of this association concept. In order to test the validity of this hypothesis, they have undertaken a program designed to determine whether external and internal plasticization is identical and to ascertain some of the structural requirements for suitable comonomers.

In this paper is described the overt effect on a selected set of physical properties produced by copolymerizing vinyl chloride with increasing amounts of each of the homologous straight-chain vinyl alkanoates. Comparative data for externally plasticized polyvinyl chloride are also presented, and the differences and similarities between the two methods of plasticization are discussed. In future work, the authors expect to eliminate the uncertainties ascribable to the difference in chemical structure of the external plasticizer and the comonomer by using as comonomers compounds which are also capable of functioning as external plasticizers. In addition, they plan to prepare compositionally homogeneous copolymers to determine whether heterogeneity has an adverse effect. Finally, they will attempt to relate any differences observed between external and internal plasticization to quantitatively determined differences in the molecular mechanisms of response to deformation by the two systems of plasticization (10, 17).

## EXPERIMENTAL

**Preparation of Copolymers.** The preparation of copolymers of vinyl chloride with vinyl esters other than vinyl acetate is briefly described in patents by Reppe (25) and in a report by Fikentscher (18). The literature on the preparation of polyvinyl chloride and copolymers of vinyl chloride and vinyl acetate is much more complete. A general review of this subject was made by Schildknecht (26).

**Reagents.** Vinyl chloride was obtained in cylinders from commercial sources and was purified by simple distillation using a cold-finger condenser cooled by solid carbon dioxide. Because several cylinders appeared to contain some volatile inhibitor, no cylinder was used unless the vinyl chloride obtained from it polymerized to the extent of at least 80% in 48 hours at 50° C. in suspension in 1% polyvinyl alcohol solution and in the presence of 0.039 mole % benzoyl peroxide.

Vinyl stearate was prepared by vinylation of stearic acid with acetylene in the presence of a zinc stearate catalyst at 165° C. and at a pressure of 200 pounds per square inch gage (13). A commercial grade of stearic acid assaying at least 95% stearic acid and containing less than 1% unsaturates was used. The vinyl stearate met the following specifications: iodine number 80 minimum to 82 maximum; melting point, 34° C. minimum; refractive index,  $n_D^{20}$  1.4419 minimum to 1.4425 maximum; and when heated for 4 hours under a nitrogen atmosphere at 70°  $\pm$  2° C. in the presence of 0.25 weight % of benzoyl peroxide, it yielded a polymer having a minimum refractive index  $n_D^{20}$  1.4540.

Vinyl acetate was obtained by distillation of the commercial product. Other vinyl esters were obtained by the method of Swern and Jordan (27).

Polyvinyl alcohol (98.5 to 100% hydrolyzed, number average molecular weight 40,000), sodium dioctyl sulfosuccinate, and sodium 2-methyl-7-ethylundecane-4-sulfate were obtained from commercial sources and used without further purification.

Benzoyl peroxide and potassium persulfate, reagent grade from commercial sources, were used as initiators without purification.

**Recipe for Suspension Polymerization.** The following general recipe (Recipe A) was used for preparing copolymers in suspension:

Monomer mixture, grams	200
1% aqueous solution of polyvinyl alcohol or sodium dioctyl sulfosuccinate, ml.	400
Benzoyl peroxide, mole %	0.039
Time of reaction, hours	48
Temperature, ° C.	50 $\pm$ 3
Yield, %	Approximately 90

These conditions were determined by studying the effect of initiator concentration, time, and temperature of polymerization on the yield, molecular weight, and mechanical properties of polyvinyl chloride produced in homopolymerization. The following observations and conclusions were made:

Of several initiator concentrations used for polymerization at 40° and 50° C. and for polymerization periods of 24 and 48 hours, 0.039 mole % benzoyl peroxide was the lowest initiator concentration which consistently gave yields in the order of 90% in 48 hours at 50° C.

Doubling the initiator concentration from 0.020 to 0.039 mole % (Table I) did not seriously decrease the degree of polymerization. A more pronounced effect on the degree of polymerization was exerted by the vinyl stearate content of the mixture than by initiator content (Table II). The degree of polymerization decreased from 1000 to 446 as the content of vinyl stearate was increased from 0 to 25 mole %. Copolymers prepared in emulsion showed a higher degree of polymerization.

The mechanical properties of polyvinyl chloride prepared at 50° C. in the presence of 0.039 mole % of benzoyl peroxide for 48 hours are similar to those of commercial polymers (Table III).

**Table I. Effect of Initiator Concentration on Degree of Polymerization of Polyvinyl Chloride<sup>a</sup>**

Benzoyl Peroxide, Mole %	Degree of Polymerization	
	Number average <sup>b</sup>	Weight average <sup>c</sup>
0.020	1000	3000
0.039	1000	2450
0.50	770	1330

<sup>a</sup> Recipe A.

<sup>b</sup> Molecular weight determined osmotically using Fuoss-Mead osmometer and tetrahydrofuran as solvent.

<sup>c</sup> Molecular weight determined by light scattering using Brice-Phoenix photometer and tetrahydrofuran as solvent.

**Table II. Effect of Vinyl Stearate Content on Degree of Polymerization in Copolymerization of Vinyl Chloride with Vinyl Stearate**

Vinyl Stearate, Mole %	Degree of Polymerization	
	In monomer mixture	In copolymer
	Suspension Copolymers <sup>c</sup>	
0.0	0.0	1000
5.0	4.2	2500
10.0	8.5	2260
15.0	12.6	994
25.0	19.8	446
	Emulsion Copolymers <sup>d</sup>	
2.5	2.5	845
5.0	4.8	810
15.0	14.3	725

<sup>a</sup> Molecular weight determined osmotically using Fuoss-Mead osmometer and tetrahydrofuran as solvent.

<sup>b</sup> Molecular weight determined by light scattering using Brice-Phoenix photometer and tetrahydrofuran as solvent.

<sup>c</sup> Recipe A.

<sup>d</sup> Recipe B.

**Table III. Mechanical Properties of Polyvinyl Chloride**

Polymer Source	Tensile Strength <sup>a</sup>	Modulus of Elasticity under Tension <sup>a</sup>	Heat Distortion Temp., ° C. <sup>b</sup>
Standard recipe <sup>c</sup>	6900	437,000	80.5
Commercial polymer	7200	442,000	81.9

<sup>a</sup> (2) using bar specimen 1  $\times$  0.25  $\times$  5 inches.

<sup>b</sup> (3).

<sup>c</sup> Suspension polymer recipe A.

**Recipe for Emulsion Polymerization.** Although many emulsifiers can probably be used with vinyl chloride, the number suitable for vinyl stearate are few. The problem became one of finding an emulsifier suitable for mixtures of vinyl chloride containing up to at least 47% (15 mole %) of vinyl stearate. The following recipe (Recipe B) gave a good latex:

Monomer mixture, grams	200
Sodium 2-methyl-7-ethylundecane-4-sulfate, grams	10
Sodium chloride, grams	1 to 4
Water, grams	390
Potassium persulfate, mole %	0.039
Temperature, ° C.	50 $\pm$ 1
Reaction time, hours	24
Yield, %	95 to 97

The amount of salt added varied with the amount of vinyl stearate used. One and 2 grams were used for 2.5 and 5 mole % of vinyl stearate, respectively, and 4 grams for 10 to 25 mole %. The amount required may also vary with the unknown amount of salt present in the particular sample of the commercial emulsifier. The amount of salt used was critical because, in some cases, variation of 0.5% in its concentration in the solution resulted in failure to obtain emulsification. The function of the salt is not understood, but it may be involved in control of the critical micelle concentration of the emulsifier, because in one instance when a high emulsifier concentration (5%) was used, no salt was needed. In the preparation of polyvinyl chloride, no salt was used.

**Polymerization Procedure.** The polymerizations were conducted in crown-capped pressure bottles. (A 32-ounce soft-drink bottle is suitable.) The dispersant or emulsifier solution, the initiator, and the vinyl stearate were placed in the bottle, the mixture was frozen to about  $-20^{\circ}\text{C}$ ., and a slight excess of vinyl chloride was added. When the excess had evaporated, displacing the air present, the bottle was capped and allowed to warm slowly to about  $5^{\circ}\text{C}$ . The cap had a small hole in its center (which served as a safety vent) and had a compound liner of cellophane, plasticized polyvinyl chloride, and tin foil with the cellophane in contact with the contents of the bottle. The bottles were heated and agitated in a large thermostated bath (23).

After the elapse of the heating period, the bottles were cooled to room temperature, the unreacted vinyl chloride was vented by piercing the liner through the safety vent, and the polymer mixture or the latex was removed. When sodium dioctyl sulfosuccinate was used as the dispersant, a small amount of the polymer was present in emulsion and was recovered by salting out. When the copolymers were prepared in emulsion, they were isolated by freezing the latex and thawing the mixture in preference to salting out or acidification techniques because of the greater ease of filtration and washing. For ease of operation, the copolymers were placed in a cotton cloth bag and separated from the aqueous phase. The bags were closed and the adhering dispersant or emulsifier was removed by tumbling the bags in water in a household washing machine. The copolymers were then extracted four times with refluxing methanol (5 ml. per gram) to remove all unused vinyl stearate. (That extraction probably removed all vinyl stearate was shown by evaporating each of the extracts to dryness and analyzing the residue for vinyl stearate. The amount of vinyl stearate found decreased with each extraction to a trace in the final extract.) It is probable that in commercial practice, extraction will be unnecessary if the conversion is carried to above 95%, but in the present work, it was necessary to obtain a monomer-free copolymer to eliminate the possibility of external plasticization.

The dried copolymers were analyzed for chlorine content and their vinyl stearate contents were calculated from figures plotted from the equations

$$\text{Weight \% vinyl stearate} = 100 - 1.763 \times \% \text{ chlorine}$$

$$\text{Mole \% vinyl stearate} = \frac{100 - 1.763 \times \% \text{ chlorine}}{100 + 6.993 \times \% \text{ chlorine}} \times 100$$

For a given initial monomer mixture, the vinyl stearate content varied with the percentage conversion. Found compositions of some typical copolymers are shown in Table IV.

**Table IV. Composition of Copolymers of Vinyl Chloride with Vinyl Stearate Prepared in Suspension**

In monomer mixture, mole %	Vinyl Stearate		Copolymer Formed, %
	In Copolymer Mole %	Wt. %	
2.5	2.1	9.7	87.6
5.0	4.2	18.0	90.3
7.5	6.7	26.3	90.4
10.0	8.9	32.7	88.4
12.5	10.6	37.1	93.7
15.0	12.6	41.7	94.7
17.5	14.8	46.3	88.3
20.0	16.2	48.9	88.7
25.0	19.8	55.5	76.8

**Physical Evaluation of Copolymers.** The copolymers were characterized by the following physical tests.

**MECHANICAL PROPERTIES.** The tensile strength, modulus of elasticity under tension, 100% modulus, and per cent elongation at rupture of copolymers having a high tensile strength were measured (2), using a bar specimen whose dimensions were  $1 \times 0.25 \times 5$  inches; for copolymers having low tensile strengths, an ASTM method (6) was used.

Flexural strength and modulus of elasticity under flexure were measured (5).

Flexural stiffness at  $73^{\circ}$  and  $39^{\circ}\text{F}$ . was measured (4).

**THERMAL PROPERTIES.** The milling temperature was determined by inserting a thermocouple into the polymer during milling.

The heat distortion temperature was determined (3).

Second-order transition temperatures were determined dilatometrically (9).

The brittle temperature was determined as the Clash-Berg (12)  $T_g$  temperature.

**VISCOELASTIC AND VISCOUS PROPERTIES.** The long-time creep behavior of the copolymers was studied by the method of Aiken and coworkers (7), except that the test specimens were prepared from a milled sheet rather than by casting from solution. One part of lead carbonate and 0.5 part of stearic acid were added per 100 parts of copolymer as a stabilizer and as a release agent, respectively.

The bulk viscosity of the copolymers was studied by the parallel-plate plastometer method of Dienes and Klemm (15).

**SOLUBILITY PROPERTIES.** Qualitative solubilities in common solvents were determined. The effect of reagents was studied by the ASTM procedure (1).

## RESULTS

**Mechanical Properties.** In Table V typical data obtained in the determination of the mechanical properties of some copolymers are listed. Composition appeared to be the chief factor influencing the value of these properties. As the vinyl stearate content was increased from about 2 to about 20 mole %, the tensile strength, the modulus of elasticity under tension, the 100% modulus, the flexural strength, the modulus of elasticity under flexure, and the flexural stiffness decreased progressively while the per cent elongation increased. When the vinyl stearate content was increased to about 25 mole %, the tensile strength and the flexural stiffness increased from the 20% level and the per cent elongation decreased sharply. (This increase in stiffness and decrease in elongation are probably due to the appearance of side chain crystallinity (24), since a first-order transition temperature,  $26.5^{\circ}\text{C}$ ., was observed in a copolymer containing 19.8 mole % vinyl stearate.) The data reveal, further, that a rough separation of the copolymers into two classes may be made: Copolymers containing 10 to 25 weight % vinyl stearate are essentially rigid materials, while those containing 30 to 50 weight % vinyl stearate are essentially flexible.

In order to compare structural plasticization with external plasticization, a study was made of the effect of progressively increasing the amount of di-2-ethylhexyl phthalate (DOP) in polyvinyl chloride on the mechanical properties of the resulting composition. The data in Table VI show that an approximate parallelism exists between the effect of increasing the vinyl stearate content and the effect of increasing the di-2-ethylhexyl phthalate content. Of particular interest is the parallelism in the effect of a temperature change ( $73^{\circ}$  to  $39^{\circ}\text{F}$ .) on flexural stiffness. An essentially rigid copolymer or an underplasticized composition showed only a slight change in stiffness (from 226,000 to 275,000 pounds per square inch, and from 214,000 to 327,000 pounds per square inch, respectively) while a flexible copolymer or a well plasticized composition showed a much greater change (from 20,500 to 110,000 and from 11,000 to 82,000 pounds per square inch, respectively).

The variation of the stiffness of several copolymers over a large temperature range is shown in Figure 1. As a reference and for comparison purposes, the variations in stiffness for Vinylite

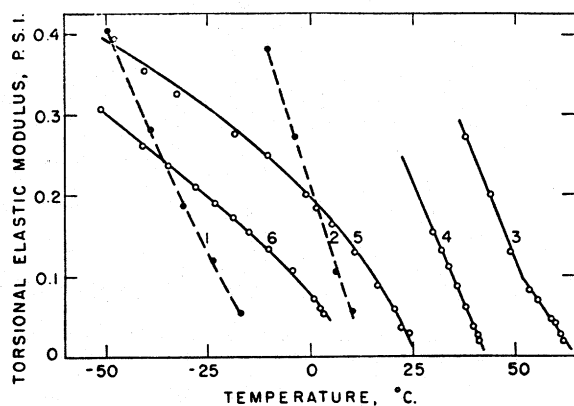


Figure 1. Temperature dependence of modulus of elasticity of copolymers of vinyl chloride and plasticized polyvinyl chloride compositions

1. VYDR + 35% DOP
2. VYDR + 35% TCP
3. Copolymer, 11.5% vinyl stearate
4. Copolymer, 19.8% vinyl stearate
5. Copolymer, 34.3% vinyl stearate
6. Copolymer, 45.2% vinyl stearate

VYDR containing 35% di-2-ethylhexyl phthalate and 35% tricresyl phosphate (TCP) are also shown. The copolymer containing 11.5% vinyl stearate shows an abrupt change in  $dE/dt$  at about 54° C. In general, below the transition temperature, as the vinyl stearate content of the copolymer is increased,  $dE/dt$  decreases. In the range tested,  $d^2E/dt^2$  is zero for the copolymers containing 11.5 and 19.8% vinyl stearate but is negative for those containing 34.3 and 45.2% vinyl stearate. These data are plotted on a semilog scale in Figure 2.

Although the vinyl stearate content appeared to be the principal factor determining the value of the mechanical properties of the copolymers, the method of preparation appeared to have some secondary influences. Thus, the copolymer (Table V) containing 35.3% vinyl stearate (prepared in emulsion) had a modulus of elasticity of 4300 pounds per square inch whereas a copolymer of similar composition, but prepared in suspension, had a modulus of 19,600. (It is probable, however, that this apparently gross difference in the values of the moduli is not reflected in a gross difference in the structure of the copolymers but is due to the fact that the measurement was made in the

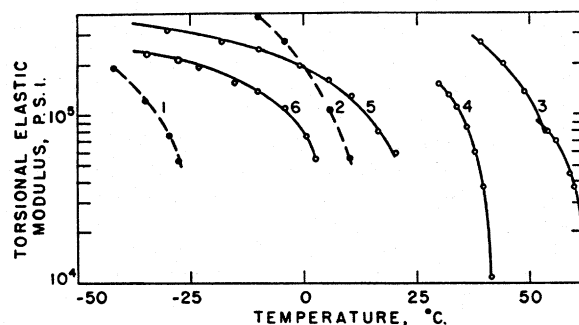


Figure 2. Temperature dependence of log of modulus of elasticity of copolymers of vinyl chloride and plasticized polyvinyl chloride compositions

1. VYDR + 35% DOP
2. VYDR + 35% TCP
3. Copolymer, 11.5% vinyl stearate
4. Copolymer, 19.8% vinyl stearate
5. Copolymer, 34.3% vinyl stearate
6. Copolymer, 45.2% vinyl stearate

transition region, where great changes in the modulus occur in a small temperature interval. Small differences in structure probably have an equally great apparent effect.) Some differences, apparently due to the method of preparation, were found in the flexural stiffness of this pair of copolymers; the emulsion copolymer had a lower stiffness at 73° F. but a higher stiffness at 39° F.

In order to determine the effect of the length of the acyl chain on the mechanical properties of copolymers of vinyl chloride and a vinyl ester, a series of copolymers of various compositions was prepared in suspension according to Recipe A, using vinyl acetate, vinyl caproate, vinyl pelargonate, vinyl laurate, vinyl myristate, and vinyl palmitate as comonomers. The compositions and mechanical properties of these copolymers are shown in Table VII. The data show that the chain length of the acyl radical and the weight per cent of the vinyl ester present are determining factors in the effect of the vinyl ester on the tensile strength, the modulus of elasticity, and the flexural stiffness of the resulting copolymer. Thus, no effect on these properties was observed when chlorine was replaced by acetate in the approximate range of 1 chlorine in 30 to 1 in 4. Progressive replacement of chlorine by a  $C_6$  acyl chain began to affect the mechanical properties when approximately every fifth atom had been re-

Table V. Mechanical and Thermal Properties of Copolymers of Vinyl Chloride and Vinyl Stearate

	Vinyl Stearate Content of Polymer														
	Prepared in Suspension, Wt. %														
	9.7	18.0	25.0	32.7	37.0	41.7	45.6	48.9	55.5	Prepared in Emulsion, Wt. %					
	2.1	4.2	6.3	8.9	10.6	12.6	14.6	16.2	19.8	2.5	4.5	10.0	14.3	19.7	24.6
Tensile strength, lb./sq. inch	6,000	4,000	2,800	1,300	...	780	...	...	...	5,500	3,400	1,500	...	...	...
Plastivertal Scott 1P-4	...	...	...	2,400	2160	1840	1570	1320	970	...	4,200	2,200	1,600	830	1,200
Elongation, %	30	30	...	200	340	260	370	420	480	...	65	310	340	460	80
Modulus of elasticity (Plastivertal) (under tension)	372,000	228,000	128,000	19,600	...	1500	1000	800	710	342,000	212,000	4,300	1,800	1,300	620
100% modulus	...	...	...	2,000	1810	1500	1000	800	710	...	...	1,800	1,300	620	...
Flexural strength, lb./sq. inch	11,200	5,500	...	2,600	...	...	...	...	...	...	...	...	...	...	...
Modulus of elasticity (under flexure)	367,000	235,000	...	90,000	...	...	...	...	...	...	...	...	...	...	...
Flexural stiffness, lb./sq. inch	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
At 73° F.	226,000	147,000	103,000	20,500	...	1300	...	...	...	270,000	164,000	6,800	4,400	6,600	18,000
At 39° F.	275,000	231,000	...	110,000	...	...	...	...	...	...	...	128,000	...	80,000	86,000
Milling temp., ° F. (av.)	265	225	275	200	180	180	90	90	90	280	220	200	150	150	80
Heat distortion temp., ° C.	55.5	44.4	...	22.1	...	...	...	...	...	...	...	...	...	...	...
Second-order transition temp., ° C.	56.5	43.7	...	...	...	...	...	...	...	...	...	...	...	...	...
Clash-Berg $T_g$ , ° C.	41.7	27.0	19.4	7.6	-11.8	-9.7	...	...	...	41.3	26.5	1.8	-7.2	-13.5	1.3

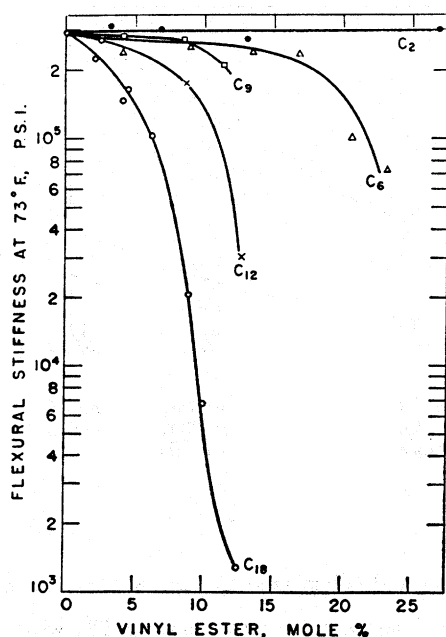


Figure 3. Dependence of flexural stiffness of copolymers of vinyl chloride and vinyl esters on composition and length of acyl chain of comonomer

placed or, considered in another way, more than one third of the volume was vinyl caproate. However, no practical flexible copolymer of vinyl chloride and vinyl caproate was obtained in the range studied. When vinyl laurate ( $C_{12}$ ) was used, flexibility was obtained in a copolymer containing about 35% (12.8 mole %) vinyl laurate, with effects on the mechanical properties appearing when 25% was present. With vinyl palmitate, flexibility was attained when about 30% was present in the copolymer. The variation of flexural stiffness with comonomer content and with chain length of the acyl radical is shown in Figure 3. The greater effectiveness of a long side chain in decreasing flexural stiffness is apparent.

**Thermal Properties.** Table V shows the change in the values of some thermal properties as the vinyl stearate content of vinyl chloride copolymers was increased. In general, these values decreased, except for an increase in the Clash-Berg  $T_f$  temperature for the copolymer containing 24.6 mole % vinyl stearate. The second-order transition temperature and the heat distortion temperature very nearly coincided. The difference in the heat distortion temperature and the Clash-Berg  $T_f$  temperature increased as the vinyl stearate content increased.

Table VI shows the decrease in the values of the thermal properties of polyvinyl chloride containing various amounts of di-2-ethylhexyl phthalate. A greater decrease in the Clash-Berg  $T_f$  temperature was produced by the same amount of this external

plasticizer than by the presence of the corresponding weight of vinyl stearate in a copolymer. With other plasticizers, as is well known, the Clash-Berg  $T_f$  temperature decreases less or more rapidly than with di-2-ethylhexyl phthalate. The milling temperature of the plasticized compositions was not affected by the external plasticizer content.

The VII shows the change in the values of some thermal properties of copolymers of vinyl chloride with several amounts of various vinyl esters. The milling temperature was not appreciably affected for the copolymer of a  $C_2$  ester at all compositions studied nor for a  $C_6$  or a  $C_8$  ester below 30%, but was markedly reduced for the compositions studied for copolymers of  $C_{12}$ ,  $C_{14}$ , and  $C_{18}$  esters. In all cases, the values of the heat distortion temperatures and of the Clash-Berg  $T_f$  temperatures were reduced with increasing ester content.

**Viscoelastic and Viscous Properties. CREEP MEASUREMENTS.** Aiken and coworkers (7) have shown that plasticizers may be differentiated on the basis of the creep behavior they produce when compounded with polyvinyl chloride. Qualitatively, a "good" plasticizer will cause a high initial response with little further long-time response. Plots of the creep data permit effective visual comparison between the behavior of two plasticizers, but they do not provide the convenience of numerical representation. The use of the  $t_3$  or  $t_{10}$  schemes of Aiken and coworkers does not permit a high initial response and low long-time creep to be differentiated from a low initial response and high long-time creep. On the other hand, characterization of a plasticizer by means of the strain per unit stress produced at a specified time [the method of Clash and Berg (12)] does not show the long-time behavior.

Table VI. Mechanical Properties of Plasticized Polyvinyl Chloride Compositions

DOP content of composition, wt. %	0	15	25	35
Tensile strength, lb./sq. inch	7200	4820	3720	2640
Elongation, %	...	35	210	270
Modulus of elasticity (under tension)	435,000	270,000	...	...
100% modulus	12,000	2,900	3120	1270
Flexural strength, lb./sq. inch	...	...	...	...
Modulus of elasticity (under flexure)	800,000	510,000	...	...
Flexural stiffness, lb./sq. inch	...	...	...	...
At 73° F.	292,000	214,000	11,000	...
At 39° F.	282,000	327,000	82,000	...
Clash-Berg $T_f$ , °C.	...	28.9	...	1.0
Milling temp., °F.	340	340	340	...
Heat distortion temp., °C.	81.9	44.9	...	...

Table VII. Mechanical and Thermal Properties of Copolymers of Vinyl Chloride and Some Vinyl Esters

	Copolymer Composition		Tensile Strength <sup>a</sup> , Lb./Sq. In.	Modulus of Elasticity under Tension <sup>a</sup> , Lb./Sq. In.	Flexural Stiffness at 73° F., Lb./Sq. In.	Milling Temp., °F.	Heat Distortion Temp., °C.	Clash-Berg $T_f$ , °C.
	Wt. %	Mole %						
Vinyl acetate	4.96	3.64	7640	419,000	314,000	340	75.0	60.7
	9.22	6.84	7600	411,000	304,000	340	71.7	55.3
	17.0	13.0	7600	423,000	272,000	300	66.8	50.0
	33.7	26.9	7900	420,000	304,000	300	55.9	40.1
Vinyl caproate	9.15	4.26	6970	394,000	242,000	300	65.8	50.3
	18.0	8.8	6430	356,000	251,000	300	54.3	37.1
	26.2	13.5	5340	318,000	244,000	280	45.8	29.8
	31.5	16.8	5300	303,000	239,000	245	...	23.6
	37.0	20.6	3200	152,000	102,000	230	...	18.1
	40.5	23.2	1510	76,000	74,000	240	...	15.9
Vinyl pelargonate	11.8	4.2	7050	385,000	281,000	300	60.5	45.4
	21.1	8.4	6000	321,000	281,000	300	47.8	31.5
	27.5	11.4	4970	283,000	210,000	300	41.3	25.0
Vinyl laurate	25.5	8.63	4840	246,000	177,000	220	...	...
	34.8	12.8	2380 <sup>b</sup>	...	30,100	150	...	...
Vinyl myristate	27.9	8.71	3160	149,000	141,000	260	...	...
	29.8	9.44	2870	138,000	107,000	240	...	...
Vinyl palmitate <sup>c</sup>	31.7	9.29	2600 <sup>b</sup>	...	27,300 <sup>d</sup>	250	...	11.7

<sup>a</sup> Tinius-Olsen Plastiversal tensile tester.

<sup>b</sup> Scott IP-4 tensile tester.

<sup>c</sup> 100% modulus, 2510 lb./sq. inch, elongation 240%.

<sup>d</sup> Stiffness at 39° F., 168,000 lb./sq. inch.



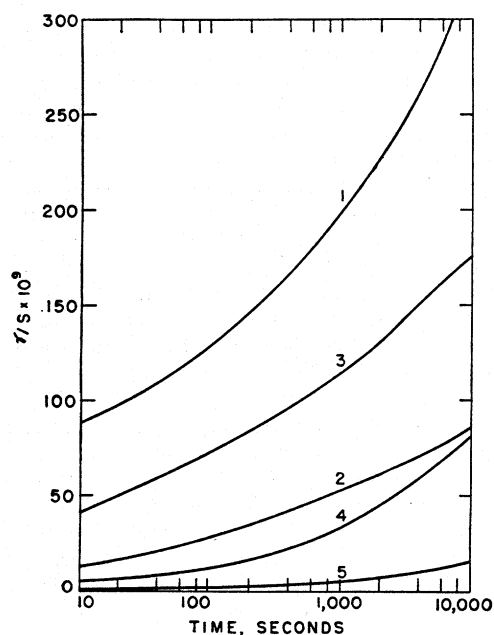


Figure 4. Creep behavior of copolymers of vinyl chloride and vinyl stearate prepared in suspension

1. 41.1% vinyl stearate at 40° C.
2. 41.1% vinyl stearate at 24° C.
3. 33.6% vinyl stearate at 40° C.
4. 33.6% vinyl stearate at 31° C.
5. 33.6% vinyl stearate at 24° C.

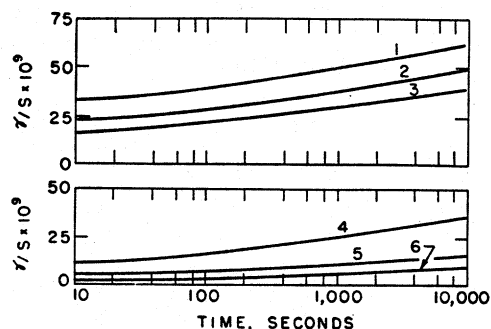


Figure 6. Creep behavior of compositions of polyvinyl chloride and dioctyl phthalate

1. 35% DOP at 40° C.
2. 35% DOP at 30° C.
3. 35% DOP at 24° C.
4. 25% DOP at 40° C.
5. 25% DOP at 30° C.
6. 25% DOP at 24° C.

In order to compare numerically the efficiency of vinyl stearate as a structural plasticizer with external plasticizers, the use of several parameters has been adopted: observed creep at 10 seconds,  $b_{10}$  (as a measure of the instantaneous response), the average slope,  $m$ , between 10 and 100 seconds (as a measure of the initial rate of change of response), and the ratio,  $m_2/m_1$ , of the average slopes between 1000 and 10,000 seconds and between 10 and 100 seconds.

Table VIII lists the creep data observed for some copolymers and plasticized compositions. The observations from which the data in Table VIII were obtained are plotted in Figures 4 to 7 as creep-log time curves. The data reveal:

Creep in copolymers containing vinyl stearate is more temperature-dependent than in externally plasticized polymers in the temperature range studied.

The initial response,  $b_{10}$ , of the copolymers is lower than that

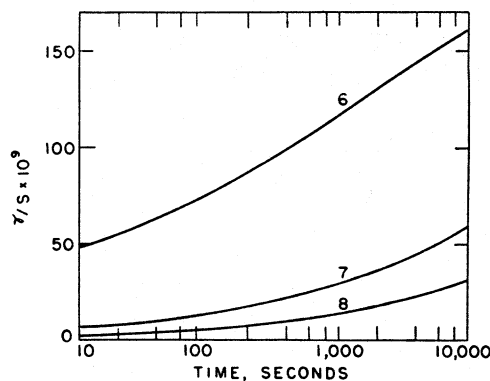


Figure 5. Creep behavior of copolymer of vinyl chloride containing 34.8% vinyl stearate prepared in emulsion

6. At 40° C.
7. At 31° C.
8. At 24° C.

of externally plasticized polymers at 24° and 31° but higher at 40°.

The initial rate of creep,  $m_1$ , increases more rapidly with temperature for the copolymers than for the externally plasticized polymers.

At 24°,  $m_2/m_1$  (a crude second derivative of creep with respect to time), for the copolymers is much higher than for externally plasticized copolymers, but as the temperature is increased,  $m_2/m_1$  decreases for the copolymers, but remains fairly constant for the plasticized polymers.

The creep curves of the copolymers, in the limited temperature range investigated, can apparently be superimposed by displacement along the log time axis, while those of the externally plasticized systems in the same temperature range cannot. A detailed investigation of the complete viscoelastic spectrum of internally and externally plasticized polyvinyl chloride may reveal the reason for this difference.

**BULK VISCOSITY.** In Figure 8 the bulk viscosities of four copolymers of various compositions are plotted as a function of temperature. The data may be fitted to the equation  $\log \eta = m \left( \frac{1}{T} \right) + b$ . The average slope,  $m$ , is  $7.45 \pm 0.53$ , which, using Flory's equation (20), gives an activation energy of 34,000 cal. per mole. The activation energies (calculated from the slopes of the lines shown in Figure 4) of compositions of Vinylite VYDR and various plasticizers are listed in Table IX. The parameter for the family of lines (for vinyl chloride-vinyl stearate copolymers) which determines the intercept,  $b$ , does not appear to be

Table VIII. Creep Behavior of Copolymers and of Plasticized Vinylite VYDR Compositions

Composition		Temp., ° C.	$b_{10} \times 10^9$	$m_1$	$m_2/m_1$
Plasticizer	%				
Vinyl stearate	33.6 <sup>a</sup>	40	41	3.3	1.8
		31	5.1	0.82	5.6
		24	1.8	0.084	12
		40	48	2.9	1.9
	34.8 <sup>b</sup>	31	6.8	0.78	3.7
		24	2.8	0.32	4.7
	41.1 <sup>a</sup>	40	88	4.6	3.1
		24	13	1.5	2.1
DOP	25	40	12	0.35	3.4
		31	4	0.20	2.5
		24	1.7	0.12	3.4
	35	40	33	0.50	2.6
		30	23	0.50	2.8
		24	15	0.55	1.6
TCP	25	40	18	1.52	0.85
		30	0.96	0.089	19.4
		24	0.62	0.015	10
	35	40	36	0.56	2.0
		30	24	0.96	1.3
		24	13	1.13	1.1

<sup>a</sup> Copolymer prepared in suspension.

<sup>b</sup> Copolymer prepared in emulsion.



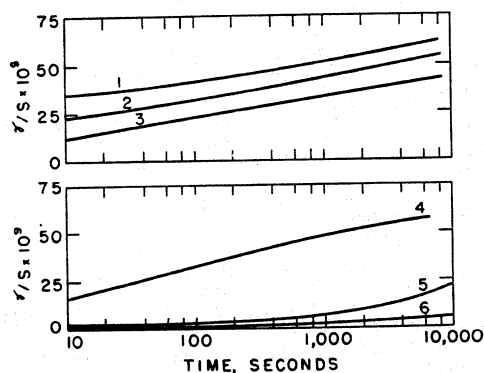


Figure 7. Creep behavior of compositions of polyvinyl chloride and tricresyl phosphate

1. 35% TCP at 40° C.
2. 35% TCP at 30° C.
3. 35% TCP at 24° C.
4. 25% TCP at 40° C.
5. 25% TCP at 30° C.
6. 25% TCP at 24° C.

the vinyl stearate content but the number average degree of polymerization [compare Flory (20)]. If  $b$  is given by  $b = K$  (degree of polymerization),  $K$  equals  $8.08 \pm 0.56$ . However, because the data are so few, this has not been established with certainty.

Table IX. Energies of Activation for Viscous Flow of Vinyl Chloride Copolymers and Plasticizer Compositions

Composition	Activation Energy, Cal./Mole
Vinylite VYDR + 25% or 35% DOP	49,000
+ 45% DOP	31,000
+ 25% or 35% TCP	47,000
+ 45% TCP	20,000
Vinyl chloride-vinyl stearate copolymers	34,000

**SOLUBILITY PROPERTIES.** The solubility of the copolymers in common organic solvents increases with increase in vinyl stearate content. A copolymer containing about 10 weight % of vinyl stearate is insoluble in aliphatic hydrocarbons and alcohols, swells in aliphatic ketones, in aromatic hydrocarbons, and in chlorinated aliphatic and aromatic hydrocarbons, and is soluble in tetrahydrofuran. A copolymer containing 20 weight % vinyl stearate is insoluble in aliphatic hydrocarbons and alcohols, swells in aromatic hydrocarbons, is slightly soluble in aliphatic ketones and chlorinated hydrocarbons, and is soluble in tetrahydrofuran. A copolymer containing about 30 to 40 weight % vinyl stearate is insoluble in aliphatic hydrocarbons and alcohols, is slightly soluble in aromatic hydrocarbons, and is soluble in ketones, chlorinated hydrocarbons, and tetrahydrofuran.

Copolymers containing about 10 and 30% vinyl stearate are not affected by 1% sodium hydroxide, 50% ethyl alcohol, or 3 or 30% sulfuric acid solutions in the ASTM test for resistance of plastics to chemical reagents (1). Cottonseed oil does not affect the copolymer containing 10% vinyl stearate, but the copolymer containing 30% vinyl stearate absorbs 40% of its weight in cottonseed oil.

### CONCLUSIONS

Although it is not yet possible to make a decisive statement on the identity of internal and external plasticization, much less to suggest any unified theory, the authors believe that the evidence presented favors a static mechanism. The obvious parallel changes in mechanical and thermal properties which are ob-

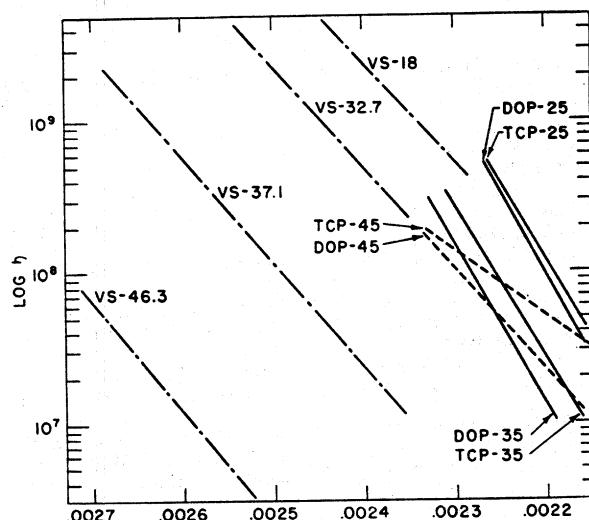


Figure 8. Temperature dependence of bulk viscosity of vinyl chloride copolymers and plasticized polyvinyl chloride compositions

served as the vinyl stearate content of the copolymers is increased on the one hand and the di-2-ethylhexylphthalate or tricresylphosphate content of the plasticized polyvinyl chloride compositions is increased on the other hand leads to the tentative conclusion that similar molecular mechanisms are operating in both systems. From Figure 3, it may be concluded that a long side chain is more effective than a short one in producing plasticization. In this respect, too, there is a parallel between internal and external plasticization (21).

Differences in behavior resulting from external as opposed to internal plasticization are found in the absolute values of the mechanical, thermal, and viscoelastic properties and in the viscosity. The reason for the differences in the absolute values of the mechanical and thermal properties of copolymers and of compositions having the same weight per cent of comonomer and plasticizer, particularly the higher Clash-Berg temperature and moduli of the copolymers, is not known. It may be conjectured that such differences may be accounted for by the difference in chemistry, by reduced crystallinity, or by association of the long comonomer side chains. Another possible cause, which is to be investigated, is the compositional heterogeneity which necessarily results from the method of preparing the copolymers. A copolymer, which analysis shows has an average of 10 mole % of vinyl stearate, for example, probably contains significant amounts of copolymers of lower and higher vinyl stearate contents. Since that fraction of the copolymers that are below their respective second-order transition temperatures have a high modulus, the contribution of the copolymers of low vinyl stearate content to the average modulus is great and is not offset by the presence of copolymers of high vinyl stearate content. In creep measurements, copolymers of vinyl chloride and vinyl stearate show greater compliance and a higher temperature dependence than do plasticized compositions. From viscosity tests it may be concluded that in internal plasticization the activation energy for flow is lower than in external plasticization.

From the viewpoint of potential use, copolymers of vinyl chloride having low vinyl stearate contents (25% or less) are rigid plastics having desirable fabricating characteristics (low milling temperature and a low viscosity-temperature coefficient). Copolymers containing 30 to 50% vinyl stearate may be useful as flexible plastics, especially where permanence of the plasticizer is an essential requirement. Both the flexible and rigid types are preplasticized, a property useful in extrusion.

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